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Relaxed-lattice model of isolated and paired isoelectronic traps in GaP

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A simple model of isolated and paired isoelectronic substitutional traps in GaP is presented that successfully explains the anomalous monotonic-in-n ordering of the nth nearest-neighbor $(\mathrm{NN})_n$-pair levels, with pair energies that vary as the inverse cube of the N-N separation. The model is a multiband deep-level theory that includes the effects of lattice relaxation around the impurities. It is predicted that $(\mathrm{Bi,Bi})_n$ pairs will not exhibit the monotonic-in-n ordering of NN_n pairs, that $(\mathrm{Bi,Bi})_1$ and $(\mathrm{Bi,Bi})_2$ will be resonant with the valence band, and that hydrostatic pressure can drive the Bi trap into the valence band.

I. INTRODUCTION

Although luminescence associated with isoelectronic P-substitutional defects such as Bi and N in GaP has been studied for over a quarter of a century,[1-3] there still is no theory which can explain all of the following facts: (i) isolated $\mathrm{Bi_P}$ produces a deep hole trap $\simeq 40$ meV above the valence-band maximum,[4,5] (ii) isolated $\mathrm{N_P}$ produces an electron trap 11 meV below the conduction-band minimum,[2] (iii) luminescence associated with $(\mathrm{Bi,Bi})_n$ pairs is not observed, and (iv) discrete luminescence lines associated with $(\mathrm{N,N})_n$ pairs are observed with the energy of the nth nearest-neighbor pair being simply related to the separation R_n between the two N atoms in the pair:

$$E(\mathrm{NN}_n) \simeq E(\mathrm{N}) - \beta R_n^{-3} \quad \text{for } n \geq 2 \ .$$

Here NN_n refers to the nth nearest-neighbor pair (with both N impurities on anion sites), $E(\mathrm{N})$ is the energy of isolated N, and β is a constant. Indeed, existing theories have been incapable of satisfactorily describing the observed ordering of the NN_n-pair levels, and do not even predict the observed monotonic variation with the separation R_n (or the neighbor number n).

In this paper we shall assume the accepted viewpoint that the isoelectronic trap levels are deep levels[6-8] due to the central-cell potentials of N and Bi, and we shall demonstrate that (i) a strain-free model cannot explain the observed monotonic-in-n behavior of the NN_n-pair lines, namely, if the impurities and host atoms are assumed to occupy sites on the undistorted lattice (i.e., if the effects of strain due to the size mismatch of impurity and host are neglected), then the energies of the NN_n-pair lines are not monotonic functions of n or R_n, and (ii) if strain is incorporated in a simple model, then all of the above unexplained facts can be easily understood.

The successful theories of the prototypical isoelectronic trap, isolated substitutional N in GaP, have all assumed that virtually the entire defect potential is localized in the central cell; the theories differed, however, in the number of host bands significantly mixed into the chemical bonds of this defect. The earlier theories, notably by Faulkner[3] and by Hsu *et al.*,[9] employed only one band until Swarts *et al.*[10] demonstrated that the natural defect potential had a strength so large ($\simeq 7$ eV) that a multiband model is necessary to renormalize the defect potential. It is now generally accepted that the minimum number of bands required to produce the sp^3 chemical bonding is eight: The N trap level is a "deep" level originating from the central-cell potential, as described by the Green's-function theory of Hjalmarson *et al.*[7]

II. INADEQUACY OF STRAIN-FREE THEORIES

Efforts to extend the isolated-N theory to NN_n pairs[11] have not produced the observed monotonic dependence on n (or R_n); see Fig. 1. While this failure might appear, at first glance, to be a property of the specific theoretical models, closer examination of the theories reveals that it is a general property of models which omit the effects of lattice strain and which instead attempt to obtain the NN_n-pair energies from electronic coupling alone, while constraining the N impurities and the host atoms to sites of a perfect zinc-blende lattice. To see this, consider the Schrödinger equation for an isolated-N impurity at site $\mathbf{A}$ ($\mathbf{A}=\mathbf{0}$ or $\mathbf{A}=\mathbf{R}_n$):

$$(H_0 + V_{\mathbf{A}})\phi_{\mathbf{A}} = E(\mathrm{N})\phi_{\mathbf{A}} \ .$$

Here $\phi_{\mathbf{A}}$ is the deep-level wave function of an isolated-N impurity at site $\mathbf{A}$, and $V_{\mathbf{A}}$ is the defect potential. For an NN_n pair, with one N impurity at the origin and the other at $\mathbf{R}_n$, the Schrödinger equation is

$$(H_0 + V_0 + V_{\mathbf{R}_n})\Phi = E(\mathrm{NN}_n)\Phi \ ,$$

with approximate bonding and antibonding orbitals

$$\Phi \simeq 2^{-1/2}(\phi_0 \pm \phi_{\mathbf{R}_n}) \ .$$

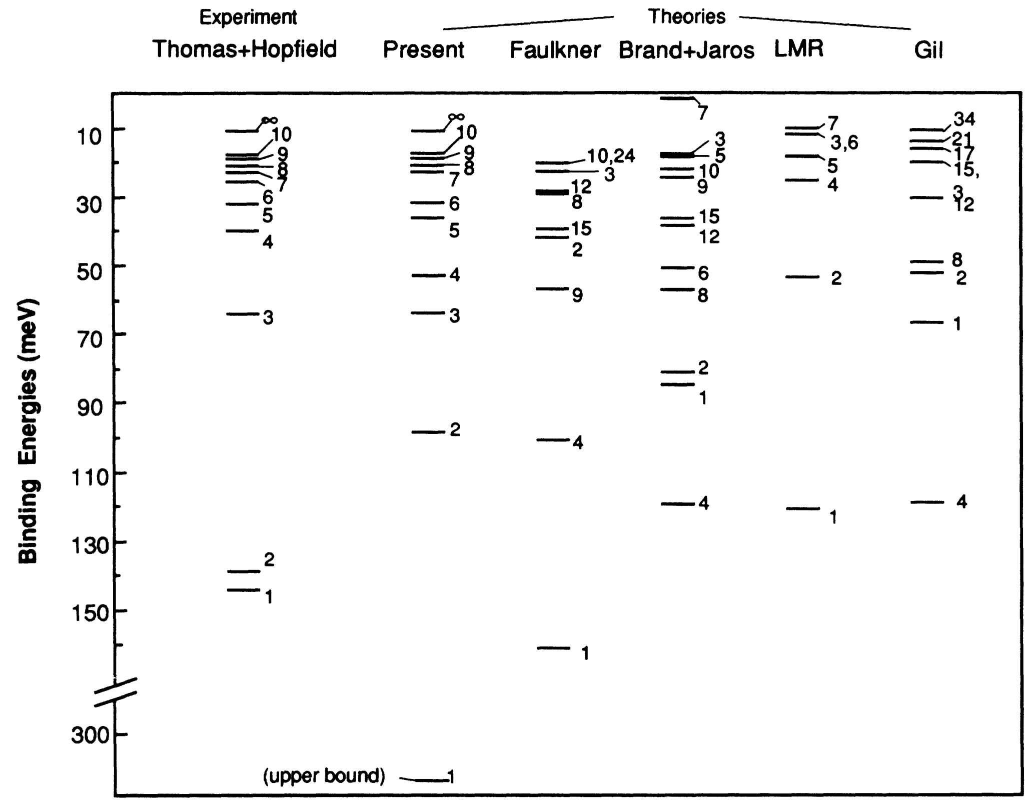

FIG. 1. Binding energies of NN_n pairs observed by Thomas and Hopfield (Ref. 2), and calculated with the present model, by Faulkner (Ref. 3), by Brand and Jaros (Ref. 16), by Li *et al.* (LMR) (Ref. 15), and by Gil *et al.* (Ref. 17). The zero of energy is the free-exciton luminescence line. Note the ordering of levels with n. The NN_1 binding energy for the present theory is an upper bound estimated by assuming $d'=d_0$; see text.

The corresponding energy is

$$E(NN_n)=E(N)+(\pm\langle\phi_0|V_0|\phi_{R_n}\rangle+\langle\phi_0|V_{R_n}|\phi_0\rangle)\times(1\pm\langle\phi_0|\phi_{R_n}\rangle)^{-1}$$

or

$$E(NN_n)\simeq E(N)\pm\phi_0(0)\phi_{R_n}(0)v_0$$

for large R_n.[12] (This approximate result agrees well with more exact calculations.) Here the overlap integral is $\langle\phi_0|\phi_{R_n}\rangle$; we have assumed that R_n is moderately large, and we have taken the defect potential to have strength v_0 and to be localized within the impurity's cell. Hence the NN-pair energy $E(NN_n)$ has the same dependence on R_n as the isolated-N deep-level wave function centered at $\mathbf{R}_n$: $\phi_{R_n}(0)$. Since this wave function is known to oscillate[13] as a function of R_n and is not monotonic, we conclude that the observed NN_n-pair energies, which are monotonic, are not determined predominantly by the electronic coupling between the two impurities.

III. ROLE OF STRAIN

Since the electronic coupling between the two N impurities in the NN_n pairs does not produce the observed monotonic-in-n ordering of the pair levels, there must be some other effect which is larger in magnitude than the electronic coupling and which produces monotonic level ordering. We shall show that elastic strain due to deformation of the host lattice in the vicinity of the defect is responsible for the observed ordering and also produces the correct magnitudes for the energies of the NN_n pairs.

We are not the first to suggest strain as the mechanism primarily responsible for the NN_n-pair energy levels in GaP. Twenty years ago Allen[14] proposed that strain, and consequentially deformation potentials, determined the NN_n-pair binding energies in GaP. His theory fell into disfavor, however, because his N-related levels were rigidly attached to the conduction band edges and would have preserved their energies, with respect to the conduction minimum in $GaAs_{1-x}P_x$ as the alloy composition x varied—contrary to the observations.[9] The important demonstration of Allen is that strain produces an effect *of the correct order of magnitude* to explain the NN_n-pair data. This raises the question of how the strain-free theories were able to obtain NN_n-pair energies of the correct order of magnitude, albeit incorrectly ordered: If both the electronic coupling and strain effects are of the required order of magnitude to explain the data, then a correct theory must account for the competition between these effects. However, in the two multiband theories, namely those of Li *et al.*[15] and Jaros and Brand,[16] the coupling between N atoms or the defect potential strength is an adjustable parameter—and this parameter leads to the large apparent electronic coupling with incorrect ordering. The theories of Faulkner[3] and Gil *et al.*[17] are missing the important effects of the valence band[7] on the impurity levels. Thus the previous theories that attempted to explain the NN_n-pair energies in terms of a strain-free electronic-coupling model considerably overestimated the effect.

IV. ISOLATED IMPURITIES

We incorporate the effects of lattice deformation and strain around an isolated impurity using the widely accepted sp^3s^* tight-binding model of Hjalmarson *et al.*[7] This model successfully described the isolated-N trap in $GaAs_{1-x}P_x$ and many other deep levels in a wide variety of semiconductors. Most of the published calculations based on this model did not incorporate the effects of strain or lattice relaxation, however, although lattice distortions are easily incorporated into the nearest-neighbor tight-binding model Hamiltonian, because the various matrix elements T between orbitals centered on adjacent sites obey Harrison's scaling rule and so are approximately inversely proportional to the square of the bond length d: $T=T_0(d_0/d)^2$. Therefore, the defect-potential matrix V of, say a N_P defect in GaP, is localized to the impurity site and its four neighbors and to the basis orbitals s, p_x, p_y, and p_z (Ref. 18) centered on those sites. The impurity-site diagonal elements are the same as given by Hjalmarson *et al.* for the strain-free theory[19]

$$V_s=\beta_s[w_s(\mathrm{N})-w_s(\mathrm{P})] ,$$

and

$$V_p=\beta_p[w_p(\mathrm{N})-w_p(\mathrm{P})] .$$

Here the w's are the atomic energies in the solid, as given by Vogl *et al.*[20]

The wave function of the N deep level is dominantly hostlike and Ga-dangling-bond-like in character. Hence, the effects of host d states are well simulated by the sp^3s^* model, which is known to treat the host electronic structure well, and the relativistic effects (which are important for Bi levels) can be neglected. The nonzero nearest-neighbor off-diagonal elements of the defect potential V are obtained from the host-crystal matrix elements, scaled for the altered (inwardly relaxed) bond length of the impurity with its four neighbors:

$$V_{\text{off diagonal}}=D=T_0[(d_0/d)^2-1] ,$$

where d is the relaxed bond length and has a value between $d_0(=2.36\ \text{Å})$ and the sum of the covalent radii of N and Ga, 2.01 Å. Details of the calculational procedure for obtaining the N deep-level energy are given in Appendix A.

V. PHYSICS OF THE RELAXATION EFFECT

The qualitative physics governing the strain-relaxation effect is displayed in Fig. 2, where we use a defect-molecule model. When a Ga atom (energy ε_{Ga}) and a P atom (energy ε_P) are brought together, a bonding and an

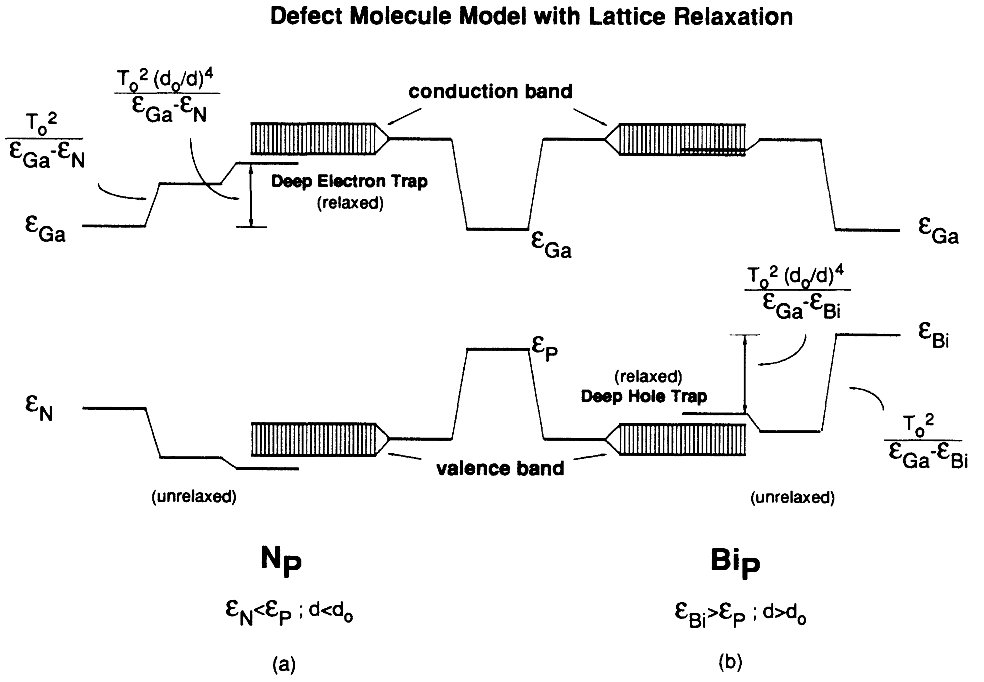

FIG. 2. Schematic illustration of the effects of the central-cell defect potential and lattice relaxation on the deep impurity levels of (a) N_P; (b) Bi_P in GaP. See text for discussion.

antibonding state will be formed. The bonding state is broadened in the crystal and forms the valence band, while the antibonding state produces the conduction band. When a N atom replaces a P atom ($\varepsilon_{\rm Ga} > \varepsilon_{\rm P} > \varepsilon_{\rm N}$), its central-cell defect potential produces a bonding hyperdeep level in or below the valence band and an antibonding deep level in the band gap. The depth of the defect potential is related to the difference in atomic energies of P and N (Ref. 7), and is $\simeq -7$ eV. Because the nearest-neighbor transfer-matrix element T is almost the same for N—Ga and P—Ga bonds, it is the larger (by $\simeq 7$ eV) energy denominator $\varepsilon_{\rm Ga}-\varepsilon_{\rm N}$ which causes the defect's bonding-antibonding splitting [of order $T_0^2(\varepsilon_{\rm Ga}-\varepsilon_{\rm P})^{-1}$ in the extreme tight-binding limit] to be smaller than the host's—leading to a deep level in the gap. Because N has a smaller covalent radius than P, the Ga collapses inward and the transfer-matrix element T increases, owing to Harrison's universal rule $T = T_0 d_0^2/d^2$ (Ref. 21). The antibonding deep level is pushed up due to such a lattice relaxation by an amount of order $T_0^2[(d_0/d)^4-1](\varepsilon_{\rm Ga}-\varepsilon_{\rm N})^{-1}$. When the impurity atom is larger than the P host atom it replaces, as in the case of Bi, the bonding deep level is pulled up in energy by approximately $T_0^2[(d_0/d)^4-1](\varepsilon_{\rm Ga}-\varepsilon_{\rm Bi})^{-1}$ as a result of relaxation.

We assume that the relaxed bond length d is a linear function of Δr, the difference between the covalent radii of the impurity and the host:[22]

$$d = d_0 + \lambda \Delta r \ .$$

The parameter λ is necessarily positive and less than unity, since the relaxation around a vacancy (the smallest-radius "impurity") does not annihilate the vacancy. We determine the precise value of λ by requiring the theory for isolated $\rm N_P$ to produce *exactly* the observed energy level, namely 11 meV below the conduction-band edge.[23,24] Note that without the lattice-relaxation effect the N level would lie 270 meV lower in energy. (See Fig. 3.) It should be emphasized, however, that λ is a phenomenological parameter whose precise value should not be overinterpreted. We have performed calculations for a variety of values of λ, using various models of the defect potential,[19] and find the physics insensitive to the detailed parametric choice.[25]

At this point the theory is completely determined for isolated impurities, and we can compute the energy level of $\rm Bi_P$—a defect that, without the lattice-relaxation effect, would give a T_2-symmetric deep-level resonant with the valence band. But Bi is larger than P and causes an outward relaxation of its neighboring Ga atoms—and this relaxation pushes the deep level up into the gap (see Fig. 3), where it lies gratifyingly close to the observed Bi energy.

According to the theory, neither $\rm As_P$ nor $\rm Sb_P$ produces a deep level in the fundamental band gap of GaP—in agreement with experiment.[26]

When hydrostatic pressure is applied to GaP, the Bi level should move down into the valence band[27] (see Fig. 4).

In GaAs, we predict that the N level descends into the fundamental band gap with increased pressure—as ob-

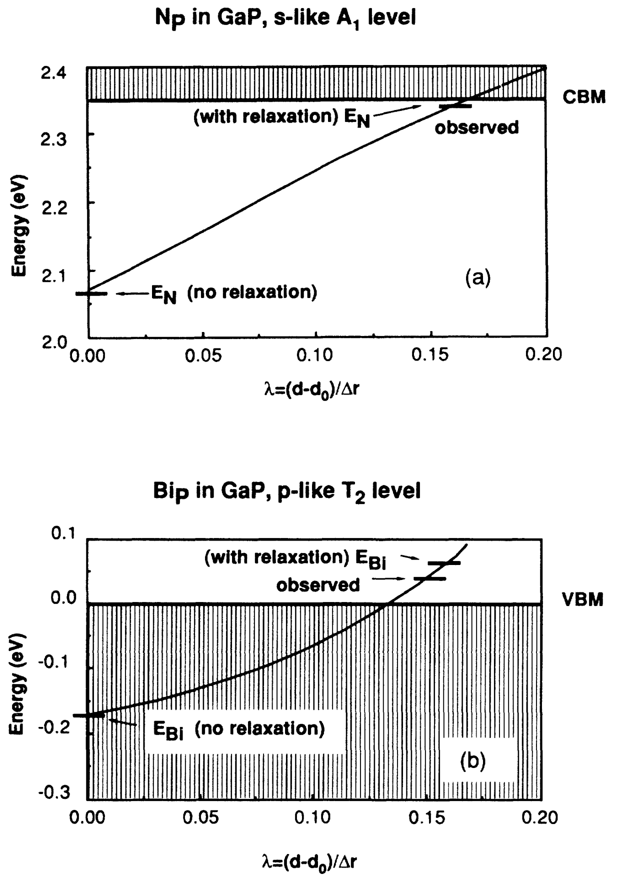

FIG. 3. Predicted results of lattice relaxation vs the parameter λ on (a) the s-like A_1 level of $\rm N_P$ and (b) the p-like T_2 level $\rm Bi_P$ in GaP. The conduction-band minimum is denoted CBM and the valence-band maximum is VBM. The shaded area corresponds to the energies of the host bands.

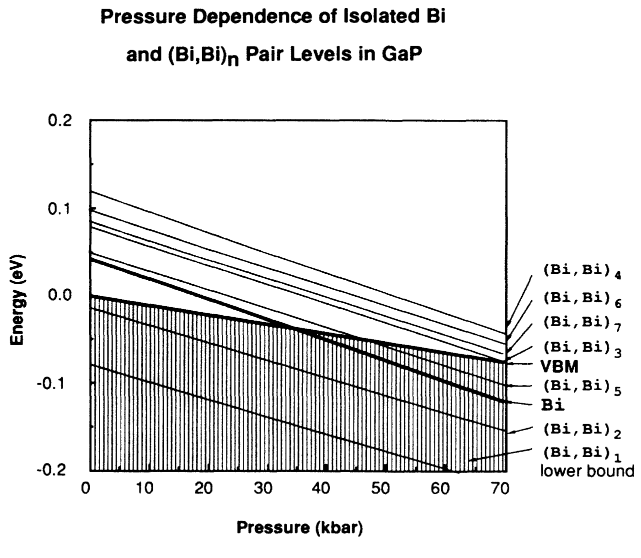

FIG. 4. Predicted dependences on pressure of the GaP valence-band maximum (VBM; dark solid line) and the isolated-Bi (dark solid line) and $\rm (Bi,Bi)_{\it n}$-paired isoelectronic traps (light solid lines).

served[28] (see Fig. 5).

This same theory, applied to Bi on an anion site in GaAs or InP, produces a level above the valence-band maximum in InP that descends into the valence band with hydrostatic pressure and a level in the valence band of GaAs that remains there—in agreement with the observations.[29] Clearly, this simple model convincingly accounts for the principal experimental facts concerning isolated isoelectronic traps in GaP and other III-V semiconductors.

VI. NN_n pairs

The model Hamiltonian for a pair of impurities, such as NN_n, can be constructed from the isolated-impurity Hamiltonian as discussed in Appendix B. One new feature arises in the case of pairs: one must (in principle) determine the relaxed bond length d' for each bond using elasticity theory.

An important point is that the strain field created by one N impurity at the origin influences the nearest-neighbor bond lengths of the second impurity at $\mathbf{R}_n$. One N, being smaller than P, causes the second N of an NN_n pair to move toward it by an amount approximately given by elasticity theory. The second N's neighboring Ga atom that is closest to the first N also moves toward the origin, causing a net elongation of the second N—Ga bond length, given by the gradient of the strain field:

$$d' = d(1 + A/R_n^3) \quad \text{for } n \geq 2 ,$$

where we have $A \simeq 2a^2\delta a$, and $a^2\delta a \simeq \pm 0.7904$ Å^3.[30] This dependence of the strained bond length on R_n^{-3} is reflected in the NN_n-pair energies. In the case of NN_1 pairs this expression for the bond length, which is based on linear-elasticity theory and the assumption that the strain fields of the two interacting N atoms do not interfere, breaks down. In this case, both N atoms will relax toward their common Ga neighbor, assuming a bond length less than d_0, GaP's bond length. Thus, for $n = 1$, we can only say $d' < d_0$. To simplify the calculation of the pair energies, we assume that a single stretched bond length d', that of the N—Ga bond closest to the first N atom, characterizes all of the N—Ga nearest-neighbor bonds of the second N. (In fact there is often a slight angular dependence to these bond lengths.) Then we obtain the energies of the NN_n pairs using the Green's-function method, as outlined in Appendix B.

The NN_n-pair energies are in excellent agreement with the data, as shown in Figs. 1 and 6. The relaxation of the strain is responsible for the R_n^{-3} and monotonic-in-n ordering of the NN_n-pair levels as observed first by Thomas and Hopfield.[2] Note that the other theories attempted unsuccessfully to explain the observed ordering in terms of electronic coupling between the two N atoms rather than in terms of strain.

It is noteworthy that the theory does *not* predict that $(\mathrm{Bi,Bi})_n$ pairs order monotonically with n or R_n. In this case the isolated-Bi states are *p*-like or T_2 symmetric and near the valence-band maximum. We find that isolated Bi lies in the gap, as observed, and that some $(\mathrm{Bi,Bi})_n$ pairs, for $n \geq 3$, lie in the gap as well. However, $(\mathrm{Bi,Bi})_1$ and $(\mathrm{Bi,Bi})_2$ lie in the valence band, due to the strain associated with its larger radius than the radius of P.

No $(\mathrm{Bi,Bi})_n$ pairs have been reported in GaP, to our knowledge. It stands to reason that for very large n these pairs will lie close to the isolated-Bi level—and so may not be resolved. For smaller n the formation of enough

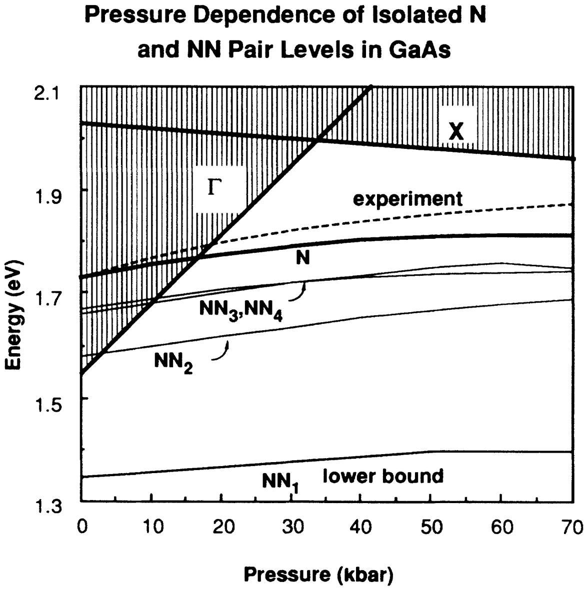

FIG. 5. Predicted dependences on pressure of the GaAs band edges Γ and X (heavy solid lines) and the isoelectronic trap N, in comparison with the data of Ref. 28. Some NN_n pairs are also shown, and have similar pressure dependences to the isolated-N level.

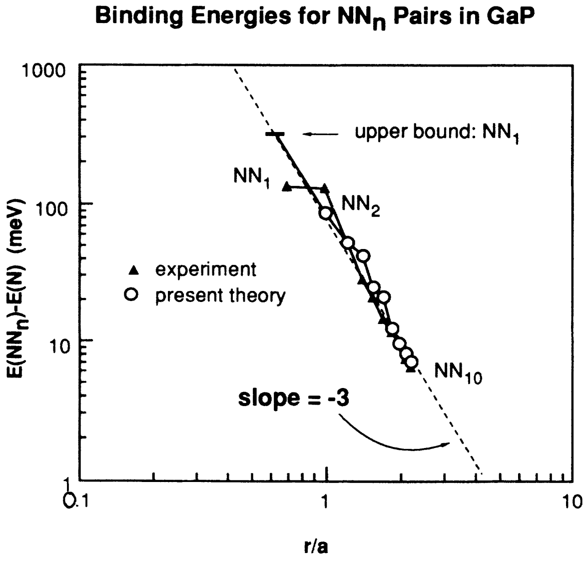

FIG. 6. Energies of NN_n-pair luminescence lines in GaP (with respect to the isolated N_P luminescence) vs pair separation R_n divided by the lattice constant of GaP, a. Open circles are the present theory for $n \geq 2$; data are denoted by solid triangles. Note the R_n^{-3} dependence caused by strain. The upper bound on the NN_1-pair energy obtained by assuming $d' = d_0$ is displayed as a bar.

pairs to observe may be limited by the Bi solubility. The interesting feature of the present theory is that it explains why $(\mathrm{Bi,Bi})_1$ and $(\mathrm{Bi,Bi})_2$ should not be observed, even if these pairs form in sufficient concentration, namely they lie outside the fundamental band gap. To a good approximation, the $(\mathrm{Bi,Bi})_n$ levels have the same dependence on hydrostatic pressure as isolated Bi, according to the theory. It would be interesting if these missing levels predicted by the theory, and their pressure dependences, were measured.

ACKNOWLEDGMENTS

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APPENDIX A: ISOLATED IMPURITY

We consider an impurity (e.g., $\mathrm{Bi_P}$) in GaP at the origin with nearest neighbors at the sites

$$\mathbf{v}_1=(1,1,1)a/4\ ,$$

$$\mathbf{v}_2=(1,-1,-1)a/4\ ,$$

$$\mathbf{v}_3=(-1,1,-1)a/4\ ,$$

and

$$\mathbf{v}_4=(-1,-1,1)a/4\ ,$$

where a is the lattice constant. On the impurity (anion or "a") site we have five orbitals $|\mathbf{0},a,s\rangle$, $|\mathbf{0},a,p_x\rangle$, $|\mathbf{0},a,p_y\rangle$, $|\mathbf{0},a,p_z\rangle$, and $|\mathbf{0},a,s^*\rangle$. Since the defect-potential matrix does not involve the excited state s^*, we ignore that orbital. The s orbital is a basis for the A_1 or s-like irreducible representation of the tetrahedral group, and the three p orbitals transform according to the T_2 representation. Another set of basis orbitals can be formed from the inward-directed sp^3 hybrids centered on the first shell of adjacent (cation or "c") sites to the impurity. They are

$$|1,A_1,s\rangle=(+|h_1\rangle+|h_2\rangle+|h_3\rangle+|h_4\rangle)/2\ ,$$

$$|1,T_2,x\rangle=(-|h_1\rangle-|h_2\rangle+|h_3\rangle+|h_4\rangle)/2\ ,$$

$$|1,T_2,y\rangle=(-|h_1\rangle+|h_2\rangle-|h_3\rangle+|h_4\rangle)/2\ ,$$

and

$$|1,T_2,z\rangle=(-|h_1\rangle+|h_2\rangle+|h_3\rangle-|h_4\rangle)/2\ ,$$

where the hybrids are

$$|h_1\rangle=(|\mathbf{v}_1,c,s\rangle-|\mathbf{v}_1,c,x\rangle-|\mathbf{v}_1,c,y\rangle-|\mathbf{v}_1,c,z\rangle)/2\ ,$$

$$|h_2\rangle=(|\mathbf{v}_2,c,s\rangle-|\mathbf{v}_2,c,x\rangle+|\mathbf{v}_2,c,y\rangle+|\mathbf{v}_2,c,z\rangle)/2\ ,$$

$$|h_3\rangle=(|\mathbf{v}_3,c,s\rangle+|\mathbf{v}_3,c,x\rangle-|\mathbf{v}_3,c,y\rangle+|\mathbf{v}_3,c,z\rangle)/2\ ,$$

and

$$|h_4\rangle=(|\mathbf{v}_4,c,s\rangle+|\mathbf{v}_4,c,x\rangle+|\mathbf{v}_4,c,y\rangle-|\mathbf{v}_4,c,z\rangle)/2\ .$$

If the defect potential matrix V associated with the impurity is confined to the central cell and its coupling is limited to first neighbors (the latter being a strain effect), then we have the nonzero matrix elements of V

$$V_1=\begin{array}{cccccccc}
|\mathbf{0},a,s\rangle & |1,A_1,s\rangle & |\mathbf{0},a,x\rangle & |1,T_2,x\rangle & |\mathbf{0},a,y\rangle & |1,T_2,y\rangle & |\mathbf{0},a,z\rangle & |1,T_2,z\rangle \\
\left[\begin{matrix} V_s \\ D_s \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{matrix}\right. & \begin{matrix} D_s \\ V_s \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{matrix} & \begin{matrix} 0 \\ 0 \\ V_p \\ D_p \\ 0 \\ 0 \\ 0 \\ 0 \end{matrix} & \begin{matrix} 0 \\ 0 \\ D_p \\ V_p \\ 0 \\ 0 \\ 0 \\ 0 \end{matrix} & \begin{matrix} 0 \\ 0 \\ 0 \\ 0 \\ V_p \\ D_p \\ 0 \\ 0 \end{matrix} & \begin{matrix} 0 \\ 0 \\ 0 \\ 0 \\ D_p \\ V_p \\ 0 \\ 0 \end{matrix} & \begin{matrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ V_p \\ D_p \end{matrix} & \left.\begin{matrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ D_p \\ V_p \end{matrix}\right]
\end{array}\ ,$$

where according to Harrison's rule,[22] the interatomic perturbation matrix elements are

$$D_s=U_s[(d_0/d)^2-1]\ ,$$

$$D_p=U_p[(d_0/d)^2-1]\ ,$$

and we have

$$U_s=T(s,s)-3T(sa,pc)\ ,$$

and

$$U_p=T(sc,pa)+T(x,x)+2T(x,y)\ .$$

Here d_0 and d are the perfect and relaxed bond lengths, respectively, and the matrix elements are the same as in Refs. 20 and 7. The deep impurity levels associated with defect are obtained by solving the secular equation

$$\det[1-G(E)V]=0 ,$$

where $G(E)=(E-H_0)^{-1}$ is the host Green's function, with matrix elements

$$G(\mathbf{R},b,i;\mathbf{R}',b',i')=\sum_{\nu,\mathbf{k}}\langle\mathbf{R},b,i|\nu,\mathbf{k})[E-E(\nu,\mathbf{k})]^{-1}(\nu,\mathbf{k}|\mathbf{R}',b',i'\rangle .$$

Here the sum is over the host bands ν and ten special points[31] in the Brillouin zone. Because of the simple form of the defect matrix, the eigenvalue equations for A_1 and T_2 levels become

$$[1-G(\mathbf{0},a,s;\mathbf{0},a,s)V_s]+[G(\mathbf{0},a,s;1,A_1,s)^2-G(\mathbf{0},a,s;\mathbf{0},a,s)G(1,A_1,s;1,A_1,s)]D_s^2-2G(\mathbf{0},a,s;1,A_1,s)D_s=0 ,$$

$$[1-G(\mathbf{0},a,x;\mathbf{0},a,x)V_p]+[G(\mathbf{0},a,x;1,T_2,x)^2-G(\mathbf{0},a,x;\mathbf{0},a,x)G(1,T_2,x;1,T_2,x)]D_p^2-2G(\mathbf{0},a,x;1,T_2,x)D_p=0 ,$$

(threefold degenerate).

This calculation has not included the effects of bond-length changes between the first- and second-nearest neighbors for two reasons: (i) we wanted to present the simplest possible model containing the essential physics of (N,N) pairs, and (ii) these effects are very small, because they affect in first-order only the hybrid orbitals centered on the nearest-neighbor sites and directed *outward* from the impurity, whereas the level positions are determined primarily by the hybridization of the impurity orbitals with the *inward*-directed hybrids.

APPENDIX B: NN_n-PAIRED IMPURITIES

For paired impurities the defect potential V_2 is a direct sum matrix

$$V_2=V(\mathbf{0})+V(\mathbf{R}_n) ,$$

where each of $V(\mathbf{0})$ and $V(\mathbf{R}_n)$ is an 8×8 matrix, and the bond lengths in these matrices are the appropriate values d' for the pair (as opposed to d). The resulting secular equation is a 16×16 matrix:

$$\det[1-G(E)V_2]=0 ,$$

which is solved for the pair energies E. The ten special points were extended to 240 points by the 24 T_d symmetry operations[15] and then were used to evaluate the Green's-function matrix elements.

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